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Complexes of a crown ether with gallium(III) iodide and indium(III) iodide

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The diethyl ether adducts $Et_2O{\cdot}MI_3$ (M = Ga or In) have been converted by reaction with the macrocyclic ether 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) into complex ionic products $[MI_2(\text{18-crown-6})][MI_4]$. Raman and IR spectra yielded the assignments: for $[GaI_2]^+$, ν_1 161; ν_2 60; ν_3 313 cm^{-1}; for $[InI_2]^+$, ν_1 150, ν_2 46, ν_3 258 cm^{-1}. X-Ray analysis of the indium compound as colourless monoclinic crystals revealed a weakly complexed $[InI_2]^+$ cation with In–I 2.617(1) and 2.619(1) Å and an I–In–I angle of 170.14(4)° threaded through the cavity of the crown ether, and a distorted tetrahedral $[InI_4]^-$ anion with the average In–I bond length of 2.708(2) Å.

Iodides of gallium(III) and indium(III) exist in the solid state as bridged dimeric molecules, $I_2M(\mu\text{-}I)_2MI_2$ (M = Ga or In).[1,2] The monomers MI_3 are Lewis acids which form the anions $[MI_4]^-$ and a range of other complexes with ligands, L. Gallium yields GaI_3L, whereas indium gives InI_3L_n, with n = 1, 2 or 3, displaying four-, five- or six-fold co-ordination.[3] Not all the MI_3 complexes are simple molecular adducts; others exist as $[MI_2L_n][MI_4]$ in which the ligand is part of a complex cation and this type is well documented in Group 13 for trihalides of Al, Ga, In and Tl.[3–5] Molecular and ionic complexes derived from MX_3 species can be of similar stability, as in the case of aluminium trichloride with tetrahydrofuran (thf) which exists as a five-co-ordinate molecule $AlCl_3(thf)_2$,[6] but also gives the ionic species $[\textit{cis}\text{-}AlCl_2(thf)_4][AlCl_4]$[7] of the same stoichiometry.

Complexes of $AlCl_3$ with crown ethers generally have ionic character, *e.g.* $[AlCl_2(\text{12-crown-4})][AlCl_4]$ (12-crown-4 = 1,4,7,10-tetraoxacyclododecane).[8] Prior examples are lacking for gallium, however indium trihalides give In_2X_6L {X = Cl, Br or I; L = dibenzo-18-crown-6 (6,7,9,10,17,18,20,21-octahydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadecane)} which are ionic according to spectroscopic results.[9] The compound $In_2Cl_6(\text{18-crown-6})$ has been obtained recently as an insoluble solid of unknown structure.[10] We have now prepared crystalline adducts of gallium(III) iodide and indium(III) iodide with 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) which prove to be of the complex ionic type, yielding structural data for the entities $[GaI_2]^+$ and $[InI_2]^+$.

Experimental

General

The compound 18-crown-6 was obtained from Acros Organics (99%). Iodine, gallium and indium were high grade materials. Schlenk-line techniques, using dry nitrogen, were employed during preparative work.

Infrared spectra were recorded as pressed discs in Polythene or KBr, using Bio-Rad FTS6000 or Perkin-Elmer Paragon 1000PC spectrometers. A 6.25 μm beam-splitter covered the range 550–40 cm^{-1}. Raman spectra were obtained with a Bio-Rad FT Raman spectrometer which gave data from 70 to 4000 cm^{-1}, and supplemented by scanning the range 10–600 cm^{-1} using a Jobin-Yvert U1000 system with a Spectra Physics 2016 argon-ion laser tuned to the green line of 514 nm at a power of 10 mW.

Preparations

$Et_2O{\cdot}GaI_3$. Analytical grade diethyl ether was dried for 48 h over freshly regenerated molecular sieves. Finely powdered gallium (0.35 g, 5 mmol) was added to a solution of iodine (1.75 g, 7.2 mmol of I_2) in dry Et_2O (10 cm^3) in a round-bottom flask. The stoppered flask was cooled in water initially, and then shaken vigorously for 45 min until the brown colour disappeared.

The compound $Et_2O{\cdot}InI_3$ was prepared similarly,[11,12] using indium (0.58 g, 5 mmol) as freshly cut shavings. The mixture became warm, and after initial cooling was shaken for 30 min until a colourless solution was obtained.

$[GaI_2(\text{18-crown-6})][GaI_4]$. A solution containing 18-crown-6 (0.1 g) in dry Et_2O (2 cm^3) was added, dropwise, to the solution (1 cm^3) of $Et_2O{\cdot}GaI_3$, prepared as above. A solid formed almost immediately as clusters of small, colourless crystals. This product was collected by withdrawing the solvent, rinsing the crystals with dry ether, and flushing with nitrogen until dry (yield *ca.* 60%) (Found: C, 12.9; H, 2.15; O, 9.55. $C_{12}H_{24}Ga_2I_6O_6$ requires C, 12.4; H, 2.1; O, 8.25%).

$[InI_2(\text{18-crown-6})][InI_4]$. A solution containing 18-crown-6 (0.1 g) in dry ether (2 cm^3) was added to the solution (1 cm^3) of $Et_2O{\cdot}InI_3$, prepared as above. The product separated as a white precipitate which was redissolved in hot acetonitrile to yield colourless crystals on cooling (yield *ca.* 70%) (Found: C, 11.6; H, 1.95; O, 7.75. $C_{12}H_{24}I_6In_2O_6$ requires C, 11.5; H, 1.95; O, 7.65%).

Crystallography

The intensity data set was collected at room temperature on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å). The ω–2θ scan was used. Three standard reflections were measured at regular 120 min intervals. Information on the collection and reduction of the data is given in Table 3. The values of I and $\sigma(I)$ were corrected for Lorentz-polarisation and absorption effects. An absorption correction was made empirically applying the ψ-scan method.[13] Reflections with $I < 3\sigma(I)$ were considered as background and excluded from all subsequent calculations. The cell dimensions were determined by least-squares refinement using the θ angles of 20 reflections in the range 18–20°. The Laue group of $[InI_2(\text{18-crown-6})][InI_4]$ is $2/m$. System-

Table 1 Vibrational spectra (cm^{-1}) of M_2I_6 crown ether complexes **1**–**3** below 500 cm^{-1}

1 $[GaI_2(crown)][GaI_4]$[a]		**2** $[InI_2(crown)][InI_4]$[a]		**3** $[InI_2(dibcrown)][InI_4]$[b]		
IR	Raman	IR	Raman	IR	Raman	Mode
396w	395vw	380vw	378w	340w		ν_L M–O
352vw	360w	332w	335w		320w	ν_L M–O
313s	310w	258s	259w	256w	260w	ν_3 MI_2^+
298w	296m	290vw	292m			Crown
280w		283w				Crown
227vs	224m	189vs	185m	194s	188w	ν_3 MI_4^-
220s	218 (sh)	180s	176w	184vs		
190vw	190w		192w			Crown
168w	161m	152w	150s	148w	150s	ν_1 MI_2^+
146w	144vs		139vs	136w	138s	ν_1 MI_4^-
110vw	110w	110w	120vw			Crown
			76w			Crown
75m	75s	62w	60m	58m	57m	ν_4 MI_4^-
60w		46m				ν_2 MI_2^+
	54m		48m			ν_2 MI_4^-

[a] crown = 18-crown-6. [b] dibcrown = dibenzo-18-crown-6 (data from ref. 9).

Table 2 Vibrational frequencies (cm^{-1}) of linear iodides, MI_2

Species	ν_1	ν_2	ν_3	Ref.
GaI_2^+	161	60	313	This work
ZnI_2	163	61	346	18
CuI_2^-	148	65	279	19
InI_2^+	150	46	258	This work
CdI_2	149	50	269	20
AgI_2^-	132	49	215	19

atic extinctions are consistent with the space group $P2_1/n$ (no. 14), which was verified by the statistical analysis of intensity distribution, packing considerations, and the successful refinement of the structure. The structure was determined by direct methods, with refinement based on *F*, using the TEXSAN package.[14] Atomic scattering factors were taken from ref. 15. Hydrogen atoms were fixed at calculated positions and included in the structure-factor calculations.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/551.

Results and Discussion

Treatment of the adducts $Et_2O\cdot MI_3$ (M = Ga or In) in diethyl ether solution with 18-crown-6 yields air-stable, crystalline solids with the composition M_2I_6(18-crown-6). Vibrational spectra (Table 1) clearly show the presence of $[GaI_4]^-$ or $[InI_4]^-$ anions, with frequencies for these species matching the original data from Raman spectroscopy of aqueous HI solutions.[16] Prior spectroscopic investigations of the series In_2X_6L (X = Cl, Br or I; L = dibenzo-18-crown-6) had indicated their likely structure to be $[InX_2L][InX_4]$.[9] Our results concur with these and the presence of a mononuclear complex cation $[InI_2(18\text{-crown-}6)]^+$ is now confirmed by X-ray crystallography (below).

There is close correspondence between the vibrational spectra of Ga_2I_6(18-crown-6) **1** and In_2I_6(18-crown-6) **2**. Hence it is probable that both compounds have the same structure, and their spectra are interpreted and assigned in Table 1 on this basis. The fundamental modes of the complex anion, $[GaI_4]^-$ or $[InI_4]^-$, appear as medium-to-strong bands. The asymmetric stretching mode is split, which is consistent with lowering of the symmetry from T_d to an irregular tetrahedral shape, as shown by X-ray analysis.

Other features of the low-frequency spectra of compounds **1** and **2** can be ascribed to the complex cations; in particular, the strong Raman band at 161 ($[GaI_2]^+$) or 150 cm^{-1} ($[InI_2]^+$) which is assigned to the symmetric stretching mode ν_1. For a linear structure the remaining modes ν_2 (bending) and ν_3 (antisymmetric stretching) should be active only in the infrared spectrum. The IR band at 313 cm^{-1} for the gallium compound, and 258 cm^{-1} for indium, is the obvious candidate for ν_3 of $[MI_2]^+$, and this attribution is supported by the fact that the ratio of these values (1.21 : 1) is exactly the same as for the corresponding mode of the $[MI_4]^-$ complexes. The presence of weak components of ν_3 in the Raman spectra can be explained by the fact that the cations are slightly bent, the I–M–I angle in the indium case being 170°.

The organic ligand contributes only a few weak features in the spectrum below 500 cm^{-1}, as established by detailed investigations of 18-crown-6 and its complex with H_3OBF_4.[17] Several such bands are identified in the present spectra. In addition, there are bands in the 300–400 cm^{-1} range which shift on changing from Ga to In, or when the present crown ether is replaced by dibenzo-18-crown-6.[9] These bands are assigned to metal-to-ligand stretching modes, and denoted by ν_L M–O in Table 1. The spectra of compounds **1** and **2** above 500 cm^{-1} are similar to those of $[H_3O(18\text{-crown-}6)][BF_4]$.[17] Principal features are a strong IR band at 1090 cm^{-1} due to C–O stretching, and a medium-intensity Raman band attributable to ring breathing of the crown ether which alters slightly from 883 cm^{-1} for the H_3OBF_4 complex to 866 for **1** and 878 cm^{-1} for **2**.

The spectra of $[InI_2(18\text{-crown-}6)][InI_4]$ are in line with those of $[InI_2(\text{dibenzo-}18\text{-crown-}6)][InI_4]$.[9] The present assignments for the $[GaI_2]^+$ and $[InI_2]^+$ cations are supported by correspondence with the modes of the iodide species with which they are isoelectronic. Table 2 shows the comparison with data for ZnI_2, $[CuI_2]^-$, CdI_2 and $[AgI_2]^-$.[18–21]

X-Ray crystallography

Fig. 1 shows the structure of compound **2**, consisting of a mononuclear complex cation $[InI_2(18\text{-crown-}6)]^+$ in association with the $[InI_4]^-$ anion. Selected bond lengths and angles for the cation, containing In(1), and the anion which contains In(2), are given in Table 4. Although $[InI_4]^-$ is distorted from full tetrahedral symmetry, the average In–I bond length of 2.708(2) Å is near that of $In[InI_4]$ (2.714 Å),[22,23] or $[InI_2(Me_2SO)_4][InI_4]$ (2.71 Å).[24] The irregularity of $[InI_4]^-$ is best attributed to crystal-packing effects since contacts between the anion and the complex cation do not appear to be significant, except in terms of electrostatic attraction.

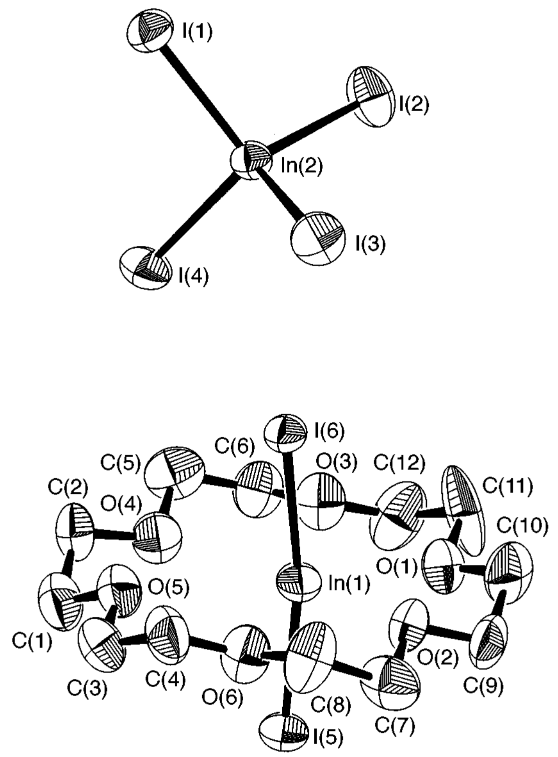

Fig. 1 Complex cation and anion of $[InI_2(18\text{-crown-}6)][InI_4]$ **2** showing the atomic labelling

Table 3 Crystal data and structure refinement of $[InI_2(18\text{-crown-}6)][InI_4]$

Formula	$C_{12}H_{24}I_6In_2O_6$
M_r	1255.39
Crystal system	Monoclinic
Space group	$P2_1/n$ (no. 14)
a/Å	12.291(2)
b/Å	13.627(1)
c/Å	17.567(2)
β/°	90.91(1)
U/Å^3	2942.0(5)
Z	4
D_c/Mg m^{-3}	2.834
Crystal size/mm	0.1 × 0.07 × 0.1
2θ Maximum/°	50.0
h, k, l Ranges	+14, +16, ±20
μ/mm^{-1}	7.885
No. unique reflections	5674
No. reflections with $I > 3\sigma(I)$	2880
No. parameters refined	236
Method of refinement	Full-matrix least squares
Decay (%)	−2.32
R	0.033
R'	0.036
S	1.58
Maximum, minimum peaks in final difference map/e Å^{-3}	0.98, −0.79

Table 4 Selected interatomic distances (Å) and angles (°) in $[InI_2(18\text{-crown-}6)][InI_4]$ **2**

Cation[a]			
In–I(5)	2.617(1)	In–I(6)	2.619(1)
In–O(1)	2.431(8)	In–O(4)	2.959(9)
In–O(2)	2.495(8)	In–O(5)	2.941(9)
In–O(3)	2.656(9)	In–O(6)	2.729(8)
I(5)–In–I(6)	170.14(4)	I(6)–In–O(1)	97.0(2)
I(5)–In–O(1)	92.5(2)	I(6)–In–O(2)	91.1(2)
I(5)–In–O(2)	95.1(2)	I(6)–In–O(3)	87.2(2)
I(5)–In–O(3)	94.9(2)	I(6)–In–O(4)	89.3(2)
I(5)–In–O(4)	83.8(2)	I(6)–In–O(5)	81.9(2)
I(5)–In–O(5)	88.4(2)	I(6)–In–O(6)	89.2(2)
I(5)–In–O(6)	86.9(2)		
Anion[b]			
In–I(1)	2.720(1)	In–I(3)	2.692(1)
In–I(2)	2.697(1)	In–I(4)	2.721(1)
I(1)–In–I(2)	107.98(4)	I(2)–In–I(3)	112.27(4)
I(1)–In–I(3)	110.17(4)	I(2)–In–I(4)	112.39(4)
I(1)–In–I(4)	104.68(4)	I(3)–In–I(4)	109.06(4)

[a] The cation contains In(1). [b] The anion contains In(2).

The cationic complex consists of the $[InI_2]^+$ unit threaded through the cavity of 18-crown-6. The I–In–I angle is 170.1°, and the In–I bond length, 2.618 Å, is distinctly less than the value (2.708 Å) associated the with $[InI_4]^-$ anion. This result is in marked contrast to the case of the cationic $[InI_2(Me_2SO)_4]^+$ complex,[24] where the In–I bonds are *longer* (2.79 and 2.81 Å) and are in *cis* configuration. Brown and Tuck[25] have recently examined the variation of indium(III)–iodine bond distances as a function of the co-ordination number of the In. For well established co-ordination numbers of four, five and six, the average In–I bond lengths are near 2.68, 2.73 and 2.83 Å, respectively, and are influenced to a lesser degree by symmetry or charge type of the particular species. Given the In–I bond length of 2.62 Å in $[InI_2(18\text{-crown-}6)]^+$, this comparison points to an effective co-ordination number for indium of less than four.

The 18-crown-6 ether complexes with MX_2 display two strong axial and six weak equatorial bonds. For $CdI_2(18\text{-crown-}6)$[26] the collinear Cd–I bonds are longer than in the isolated molecule and the Cd–O distances range from 2.69 to 2.81 Å. For $[InI_2(18\text{-crown-}6)]^+$ no data exist for the isolated InI_2^+ cation. The complex has In–O links of 2.43 and 2.49 Å to O(1) and O(2), respectively, with other distances to oxygen of 2.66–2.96 Å. The sum of the single-bond covalent radii of In and O is 2.22 Å,[4] and the observed data for indium halide complexes with oxygen-donor ligands cluster around this value, *vis-à-vis* 2.15 to 2.20 in $[InI_2(Me_2SO)_4]^+$,[24] 2.14 in $[InCl_2(Ph_3PO)_4]^+$, 2.17 in $InCl_3(Me_3PO)_3$, 2.24 in $InX_3(Me_3AsO)_3$ (X = Cl or Br), 2.20 in $InX_3(Me_2SO)_3$ (X = Cl or Br),[27] 2.18 in $InCl_3\{(Me_2N)_3PO\}_2$,[28] 2.26 in $InCl_3(thf)_2$,[29] and 2.29 to 2.33 Å in $(InCl_3)_2(dme)_3$ (dme = 1,2-dimethoxyethane).[10] The last of these complexes mimics the crown ether situation but its In–O distances are shorter, 2.29–2.33 Å. In $[TlI_2(18\text{-crown-}6)][TlI_4]$, the thallium analogue of **2**, the $[TlI_2]^+$ group has Tl–I 2.637 Å and I–Tl–I = 177.5°, and the fit of the crown ether gives Tl–O distances of 2.65–2.84 Å.[30] Unfortunately, crystals of $[GaI_2(18\text{-crown-}6)][GaI_4]$ **1** proved to be unsuitable for X-ray investigation.

Acknowledgements

We thank the Swedish Research Council for a grant in support of this work, and Mr. Per Svensson for assistance in the crystallographic study.

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Received 12*th February* 1997; *Paper* 7/01017F